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Resonant Photoemission, a variant of Photoelectron Spectroscopy, has been demonstrated to have sensitivity to aging of Pu samples. The spectroscopic results are correlated with resistivity measurements and are shown to be the fingerprint of mesoscopic or nanoscale internal damage in the Pu physical structure. This means that a spectroscopic signature of internal damage due to aging in Pu has been established.

KEYWORDS: δ-Pu(Ga), Plutonium Aging, Resonant Photoemission Spectroscopy

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1. Introduction

Scientifically, the actinides remain an unresolved subset of condensed matter physics and chemistry. The physical and electronic structures of the actinides and actinide compounds have been the subject of many important and sophisticated investigations in the recent past.[1-15] Technologically, the issue of aging is of immense significance with long term impact on public policy.[16]

Previously, we reported the observation of strong age-dependent effects in the resonant photoelectron spectroscopy (RESPES) of Pu,[17] but were unable to explain these observations. RESPES is a type of photoelectron emission in which additional emission channels are accessed along with the usual direct channel of photoemission. These additional channels are associated with core level excitations and a type of Auger-like decay. It was found that the RESPES effect was AMPLIFIED in an aged δ-Pu(Ga) sample, instead of diminished as one might expect. So, once again, Pu has exhibited a counter-intuitive effect, but this time it appears to be associated with the Pu aging process. Examples of this are shown in Fig. 1. In this report, we will demonstrate that these spectroscopic observations can be directly correlated with nanoscale disruptions of the mesoscopic ordering the Pu(Ga) physical structure.

2. Experimental

The resonant photoemission experiments were carried out at the SpectroMicroscopy Facility (Beamline 7.0)[17] at the Advanced Light Source in Berkeley, CA, USA. In the photoelectron (and x-ray absorption) measurements, the photoelectron (sample current)

intensity was normalized to the photon flux by a gold mesh drain current measured upstream.

The Pu spectroscopy experiments were performed upon an aged (10 years old) and young (2 months old) δ-Pu (Ga) alloys, each having a mass of approximately 30mg. The new Pu samples were taken from a specially purified batch of Pu metal,[17] while the aged sample was less purified. The plutonium was zone refined and vacuum distilled while magnetically levitated. The product of the purification process was α-Pu containing a total of 170 ppm impurities. A portion of the refined metal was alloyed with gallium to form the δ-phase (fcc symmetry). The sample surfaces were prepared by repeated room-temperature, sputter-annealing cycles to minimize the amount of oxygen and other impurities dissolved in the sample or at grain boundaries, in a specially designed chamber attached to the sample introduction and analysis systems on Beamline 7.0. The annealing temperature was kept at 100 °C to prevent annealing the accumulated radiological damage in the aged sample at higher temperatures. The transfer, preparation, and analysis chambers ensured that the Pu metal samples did not experience pressures greater than 10^{-8} torr. This minimized any surface contaminants that could adversely effect the soft x-ray measurements. Unless other wise specified, the valence band spectra were collected with an energy bandpass of 200meV and the core level spectra had a bandpass of 300meV.

The low temperature resistivity,[18] dilatometry,[19] and room temperature resistivity[20] experiments can each be found in its individually specified reference. Pu is highly radioactive and chemically toxic, so extreme care is required.

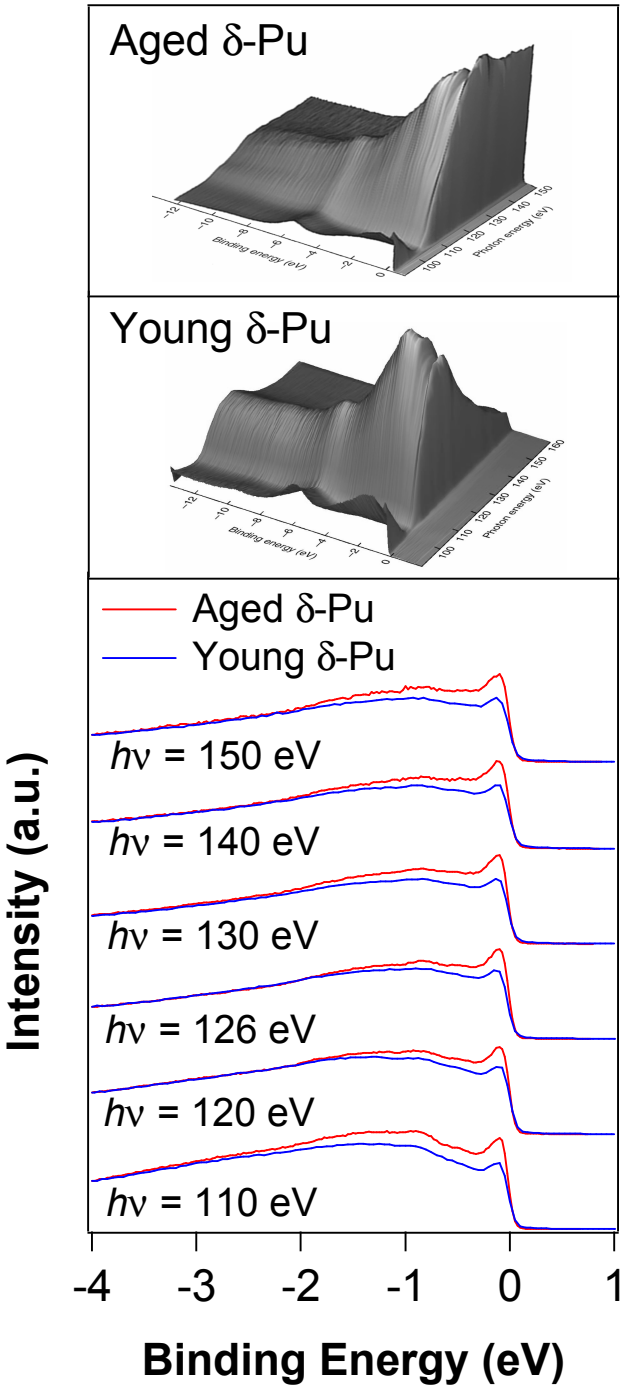

Figure 1. The RESPES results at room temperature for a young, highly purified δ-Pu(Ga) sample are compared with an aged (10 years old) δ-Pu(Ga). In the topmost panels are the pseudo-three dimensional plots, with binding energy (0 to –12 eV) and photon energy (100 to 150 or 160 eV) as the in plane axes and

the out of plane axis being intensity.[17] In the lower panels, comparison of the young and aged samples is made at specific photon energies, over the resonance regime photon energy range.

3. Results and Discussion

The conventional wisdom concerning the spectroscopy of aging in Pu was that it was difficult, if not impossible, to observe age dependent effects. An example of this is shown in Fig. 2 (a) and 2 (b). Here, the X-ray Absorption Spectroscopy (XAS) and the wide Photoemission Spectroscopy (PES)[17] of aged and young delta Pu are almost identical. X-ray absorption using total electron yield at the 5*d* threshold ($O_{4,5}$) are shown in Fig. 2 (a). The mean free path for total yield has been estimated to be on the order of 22 Å,[17] thus this is fairly bulk sensitive measurement. Although there is a small vertical offset in one of the aged spectra, denoted as (a2) in Fig. 2 (a), the overall appearances of the spectra are essentially the same. Thus it is unclear whether the spectroscopic difference in the XAS is meaningful or merely an artifact of imperfect normalization of beamline effects such as beam decay and beam shift. In PES, core levels do not reveal drastic differences between young and aged samples such as shifts in binding energy that may indicate differences in Pu 5f occupation. Thus, the XAS and PES spectral data for young and aged δ-Pu(Ga) do not exhibit any incontrovertible evidence of aging related effects. Similar results have been found for other spectroscopies. For example, Electron Energy Loss measurements of the 4d to 5f transitions in young and aged δ-Pu(Ga) produce spectra which are essentially identical with that measured for α- Pu,[14] within an uncertainty associated with the background subtraction.[21]

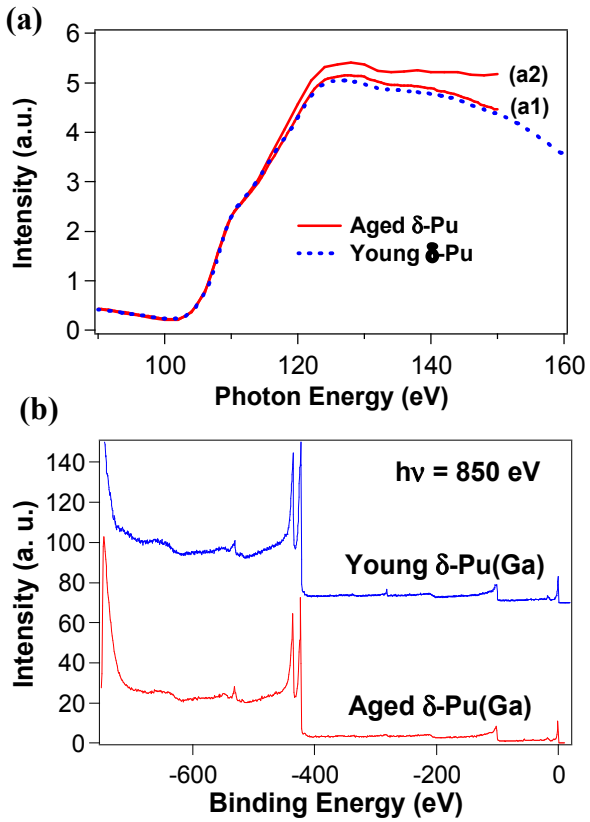

Figure 2. (a) The XAS of young and aged δ-Pu(Ga) are shown here. The instrumental bandpass was 40 meV or better throughout. Spectral scaling was made at the first edge, 100 –110 eV. Although there is a small vertical offset in one of the aged spectra, denoted as (a2), the overall appearances of the spectra are essentially the same. (b) Pu wide photoemission scans at 850 eV.[17] The bandpass was about 350 meV in these spectra.

Considering what is going on in the radioactive decay process, this absence of strong, undeniable spectroscopic indications of aging is somewhat surprising. As shown in Fig. 3 (a), the emission of an alpha particle (He^{+2}) induces a recoil motion in the newly generated U atom. Both of these processes will produce cascades of damage. As a result, radiation damage from alpha decay in plutonium occurs at a rate of ~0.1 dpa (displacement per atom) per year, while the rate of helium production is ~41.1 appm

(atomic parts per million) per year.[22] For example, each atom in the crystal lattice of plutonium is displaced from its site once every decade. Moreover, this type of damage from the alpha decay and other processes can be measured in what is essentially real-time via low temperature resistivity measurements, as recently illustrated by M. Fluss *et al*[18]. In this work, the plutonium alloy accumulated defects by low-temperature (10°K) damage-accumulation and its resistance measured after annealing at higher temperatures. As shown in Fig. 3 (b), the self-irradiated Pu sample exhibits both the negative slopes of the resistivity plots versus T(°K) and in the initial values of each plot, which diminishes with the temperature of the pre-anneal. Based on this result, the defects generated by radiation damage increase the resistivity of plutonium.

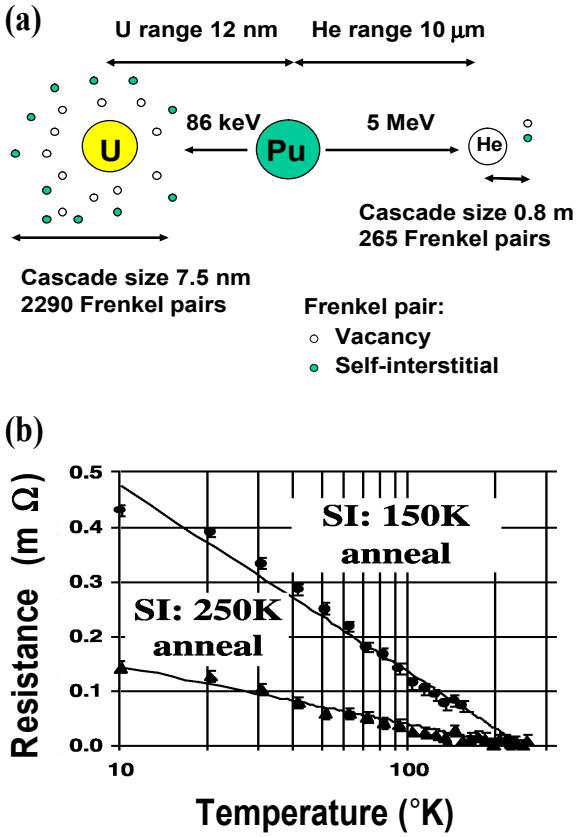

Figure 3. (a) This is a schematic of a possible Pu radiative decay.[22] (b) An example of low-temperature resistivity measurements in self-irradiated (SI) Pu samples. Two measurements are shown: the upper with a pre-anneal of 150 °K and the lower with a pre-anneal of 250°K.

Thus we return to a consideration of Fig. 1. Here, there are strong indications of an aging-driven effect, independent of the normalization scheme. In the topmost panels, there is a comparison between the young and aged δ-Pu(Ga) of the overall RESPES spectral result of each sample, using a cross normalization between individual photoemission scans based upon the photon beam intensity measurements made via an upstream gold grid. Each exhibits the sigmoidal shape of RESPES: the pre-resonance at 90 eV photon energy, the minimum of the anti-resonance at 100 eV photon energy and the high intensity of the resonance, starting at a photon energy of about 120 eV. The aged sample appears to have a much more extended resonance range, with a high intensity at the Fermi Level extending out to photon energies of 150 eV, while the young sample has a significant drop off as the photon energy moves through 140 eV, up to 160 eV. One could again raise the issue of normalization: perhaps the problem illustrated by the XAS results is also occurring here. As a test of that, an alternate normalization approach was used, where individual spectra at a specific photon energy, one each from the young and aged δ-Pu(Ga), were compared. Examples of this at photon energies of 110, 120, 126, 130, 140 and 150 are shown in the lower panels of Figure 1. Here, the pairs of spectra were normalized at energies above the Fermi Level and at a binding energy of –4 eV. It is possible to see that throughout the energy range, there is a consistent AMPLIFICATION of the intensity in the aged sample, on the scale 30% or so at the Fermi Energy (The Fermi Energy is at a binding energy of 0 eV). Changing the

lower normalization energy from –4 eV to more negative values produced essentially the same result, although the exact magnitude of the spectral differences was dependent upon the normalization energy chosen.

Obviously, the next question is "why." What is driving the differences in the resonant behavior? Logically, it must be some sort of extra-atomic effect. One possibility was MARPES, or multi-atom resonant photoemission. However, there are two problems with that interpretation: (1) the amplification effect is in the wrong direction (the amplification should be for the young, not the aged sample) and (2) earlier reports of large MARPES effects have been discredited and only much smaller effects are now asserted.[23] Alternatively, there has been a fairly recent report by Dowben of a different sort of extra-atomic effect in RESPES.[24]

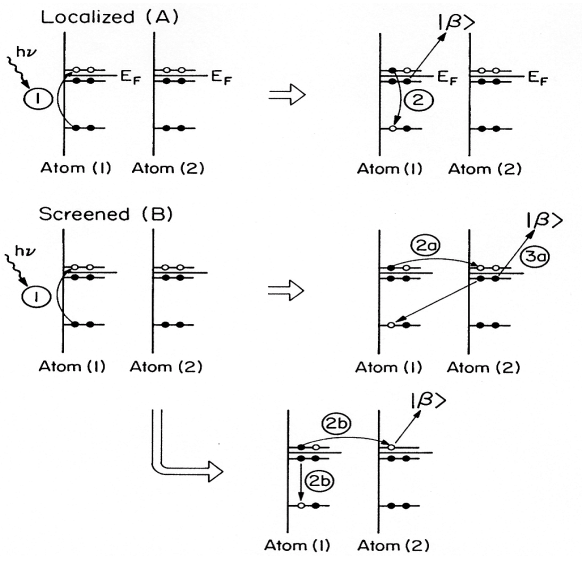

Figure 4. Intra- and extra- atomic channels of decay in the resonant photoemission process.[24] In the localized case (non-metallic), single decay channel is allowed (A). In the screened case (metallic), additional decay channels are allowed (B).

Using the manganite system $La_{0.65}Ca_{0.35}MnO_3$ or LCMO, Dowben showed that moving from a metallic phase at low temperature (T = 173 °K) to a non-metallic phase at high temperature (T = 293 °K) induced a very large increase in the resonant photoemission of the LCMO.[24, 25] In the metallic phase, there is only a very small change in intensity between the photoemission valence band spectra acquired at photon energies on resonance (55eV) and off resonance (47eV). In contrast, the spectrum acquired at the non-metallic phase showed a significant increase in the intensity of the valence band obtained with a photon energy of 55 eV. He was able to explain this in terms of extra-atomic screening.[24, 26] As shown in Figure 4, if only intra-atomic decay is allowed, then there is only one possible decay process. However, if extra-atomic decay is allowed, then there are additional channels for decay (or the lifetime of core exciton is dramatically reduced). Dowben argued that in the localized case (non-metallic) the single decay channel allowed for the continued existence of the resonant behavior, but in the screened case (metallic), the extra atomic decay channels quenched the resonant effect. This is essentially what has been observed in Pu: the highly ordered young samples have superior screening, giving rise to a quenching relative to the aged samples. Because of the mesoscopic disorder in the aged samples, the extra-atomic screening is compromised, allowing the resonant behavior to be amplified relative to the young samples.

To summarize: Increased screening quenches the RESPES, radiological damage restricts the screening in the aged sample and thus the aged sample has more RESPES.

Furthermore, it is clear that the underlying physics of the screening process and conductivity (the inverse of resistivity) would be the same. The decrease in the density of

the conduction electrons across the metal to non-metal transition coincides with a decrease in the screening process.[24, 25] Diminished screening should thus correspond to diminished conductivity and greater resistance. Hence, it should be possible to test this hypothesis using resistivity measurements as in the manganite system.[25] However, the resistivity effects in room-temperature Pu samples are different than the type of resistivity effects observed at very low temperatures, as shown in Fig. 3 (b). At room temperature, many of the sources of the low temperature effects may have been eliminated by an effective annealing at room temperature. Nevertheless, there has been strong evidence of aging effects in room temperature samples. For example, consider Fig. 5 (a), where accelerated aging samples clearly show increases in length with time and hence dosage. After 10 years of aging at room temperature, the plutonium alloy has swelled in volume by 0.09%. Thus, although these samples have been at or near room temperature, the samples are experiencing aging affects.

The effect of annealing a room temperature sample is shown in Fig. 5 (b). Both the young and aged samples were cycled first to lower (-200°C), then higher (above 300°C) and finally back to the starting temperature (about 40°C). The key effects are about 20% higher resistance at room temperature and drop in resistance during annealing above 100°C in the aged sample. As the radiological damage in the aged sample is annealed, the relative resistance drops to a value similar to the young sample. In contrast, the resistance of the young sample during the annealing is constant because of insignificant accumulation of the residual internal damage. A subsequent cooling of the annealed aged sample to 40°C does not result in a reversal of the resistivity drop but rather causes only a small increase in the relative resistance. Additional temperature cycles on the aged

sample after annealing show resistance behavior similar to that of the young sample. Clearly, the radiological damage causes greater resistance and thus the diminished screening in the aged sample near the room temperature where RESPES was measured.

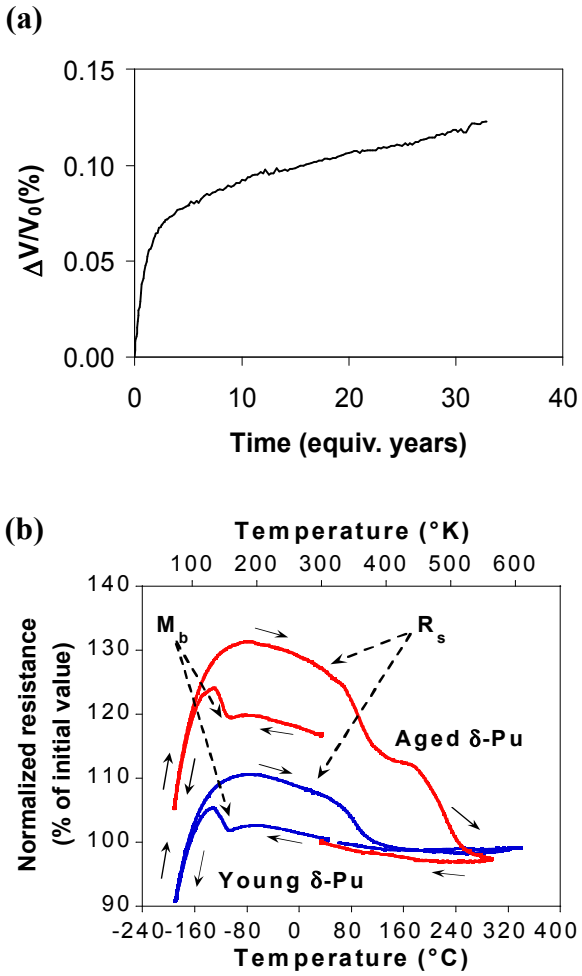

Figure 5. (a) The relative volume expansion of δ-Pu(Ga) by aging at room temperature.[19] In this case, accelerated aging was achieved by doping a ^{239}Pu sample with 7.5 weight % of ^{238}Pu. The time equivalent in regular years is shown as the x-axis. (b) Normalized resistance of a young δ-Pu(Ga) (blue) and an aged δ-Pu(Ga) (red) samples during a thermal cycle.[20] The aged sample was 18 years old. Plot also shows martensite transformation temperatures (M_b) and austenite start temperatures (Rs). The resistance scales were normalized at the final cycle temperature (about 40°C) because the annealed aged sample showed similar resistance to the young sample.

Considering the significant difference between the young and aged Pu samples, it is useful to discuss the effects of surface oxidation. Both RESPES and wide PES scans show O 2p (BE = -5eV in Fig. 1) and O 1s (BE = -529eV in Fig. 2 (b)) signals indicating presence of surface oxides. The O 1s peak is overlapped with a Pu Auger peak in Fig. 2 (b). However, it is estimated that the level of oxygen contamination is fairly limited and does not adversely affect the soft x-ray measurements.[17] If the surface oxide did contribute to the resonant enhancement, we should see a similar RESPES enhancement regardless of the sample age. However, we see much stronger resonance intensity in the aged sample. Thus, the resonant enhancement in the aged sample is from an age-dependent effect.

Finally, it is worthwhile to consider the chemical impact of doping from the decay products in the Pu samples. As the various nuclear reactions occur, daughter elements will form from the decay of the Pu sample. For example, in the alpha decay shown in Fig. 3 (a), U daughter atoms will appear. However, based upon the known half-life, it is estimated that after 10 years, less than 0.0034 % (atomic) of U will be produced in these Pu samples. Thus the concentration ratio of [U]/[Pu] is less than 10^{-4} . Hence it seems fairly unlikely that the mere presence of the dopants is sufficient to generate such effects as the RESPES amplification and resistance increase, but rather the mesoscopic scale damage caused by radioactive decay is the cause.

4. Conclusions

It has been shown that the amplified RESPES response in an aged Pu sample is due to the nanoscale damage of the aged sample. This analysis is founded upon a model of

screening developed and experimentally tested independently by Peter Dowben. Furthermore, the model's application to Pu was tested via resistivity measurements versus temperature of a room temperature sample of Pu. We now have a spectroscopic signature of aging in Pu.

Acknowledgements

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